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16. ABSTRACT

A new voltammetric membrane electrode for trace analysis of ozone was developed. The effects of stirring and temperature as well as the response time were investigated. Using a three-electrode voltammetric cell, and a gas permeable membrane, measurements were done using steady-state and pulse techniques. The advantages of the pulse technique in comparison to steady state include a fifty-fold increase in sensitivity, ability to measure in the part per billion range, and less dependence on mixing in the test solution and thickness of the polymeric membrane. The pulse technique is particularly suitable for monitoring applications since the electrode sensitivity is less dependent on the accumulation of suspended matter on the surface of the membrane, when compared to steady-state measurements. One of the main applications of this electrode system will be the control of ozonation processes based on in situ measurement of residual ozone.

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In Situ Voltammetric Membrane Ozone Electrode

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A new voltammetric membrane electrode for trace analysis of ozone was developed. The effects of stirring and temperature as well as the response time were investigated. Using a three-electrode voltammetric cell, and a gas permeable membrane, measurements were done using steady-state and pulse techniques. The advantages of the pulse technique in comparison to steady state include a fifty-fold increase in sensitivity, ability to measure in the part per billion range, and less dependence on mixing in the test solution and thickness of the polymeric membrane. The pulse technique is particularly suitable for monitoring applications since the electrode sensitivity is less dependent on the accumulation of suspended matter on the surface of the membrane, when compared to steady-state measurements. One of the main applications of this electrode system will be the control of ozonation processes based on in situ measurement of residual ozone.

The industrial application of ozone and the study of its reactions are greatly limited by the lack of an adequate sensor system capable of in situ and instantaneous measurement. This can be seen in current attempts to apply ozone as a disinfectant and oxidant in water and wastewater treatment processes. Because of its high instability, ozone must be generated on site at the treatment facility and immediately applied by injecting a freshly prepared ozonated water. Dosage regulation is usually done manually and is controlled by measuring dissolved ozone in the contactor outlet. Available methods for the analysis of ozone lack sensitivity, selectivity, and/or the rapidity required for continuous automatic control (*1–4*). Effective applications of ozone are largely dependent on the availability of an in situ ozone sensor for the automatic control of ozone generation.

Electrochemical techiques provide the unique possibility for in situ, continuous, and automated measurements of ozone. This paper describes a voltammetric membrane electrode system capable of in situ measurement of ozone in the part per billion range and suitable for monitoring processes control applications. The application of the pulse technique provides the advantages of higher sensitivity and lower detection limits vis-a-vis steady-state measurements. Both steady-state and pulse techniques are discussed in this paper.

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THEORY

The electrochemical reduction of ozone on solid metal electrodes has been reported by several authors (*5–13*). In acidic media, using a ring-disc electrode, Johnson et al. (*6*) verified that the electrochemical reduction of ozone is as follows:

$$O_3 + 2e + 2H^+ \rightarrow O_2 + H_2O \qquad (1)$$

The cathodic reduction of ozone in alkaline media was reported by Fabjan (*11*), who also repeated the earlier work of Johnson et al. (*12, 13*). Recently, Johnson and Dunn (*14*) reported the development of an ozone amperometric membrane electrode utilizing a microporous membrane in contact with a gold electrode.

The diffusion current equation for voltammetric membrane electrodes has been reported by Mancy et al. (*15*). Under steady-state conditions, the diffusion current can be expressed as:

$$i_{ss} = nFA \frac{P_m}{b} C \qquad (2)$$

where i_{ss} = current at steady state, amperes; n = number of electrons equivalent per mole of ozone, equiv/mol; F = the Faraday, Cs/equiv; A = cathode area, cm^2; P_m = membrane permeability coefficient for ozone, $cm^2\ s^{-1}$; $P_m = K_m D_m$, where K_m is ozone partition coefficient at membrane-solution interface, nondimensional, and D_m is membrane diffusivity coefficient for ozone, $cm^2\ s^{-1}$; b = membrane thickness, cm; and C = ozone concentration, mol cm^{-3}.

In this case it is assumed that the activity coefficient is equal to unity. A detailed derivation and description of the theory of diffusion current for two-layer systems is found in the original article.

Using pulse voltammetry, the transient current response at short intervals of polarization where membrane permeability is limiting, has been reported by Mancy et al. (*15*) to be

$$i_t = nFA \left(\frac{P_m}{\pi t}\right)^{0.5} C\left\{1 + 2\sum_{n=0}^{\infty} \exp \frac{-n^2 b^2}{D_m t}\right\} \qquad (3)$$

where D_m = membrane diffusion coefficient, $cm^2\ s^{-1}$; and t = polarization time, s.

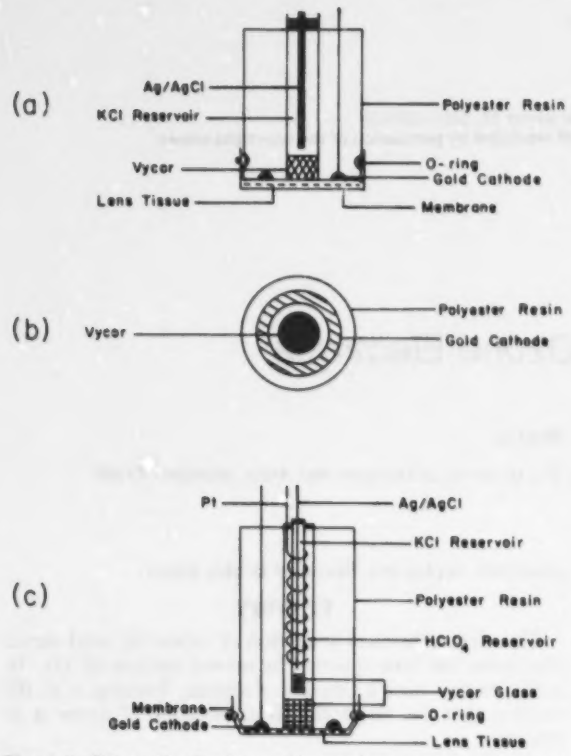

Figure 1. Schematic of voltammetric membrane ozone probes. (a) Two-electrode system. (b) Bottom view of the electrode. (c) Three-electrode system

At small values of t, estimated for this electrode system to be $t < 0.19\ b^2/D_m$, Equation 3 is reduced to

$$i_l = nFA\left(\frac{P_m}{\pi t}\right)^{0.5} C \qquad (4)$$

The utilization of the pulse technique with voltammetric membrane electrodes offers a unique approach to trace analysis, where the membrane serves for in situ sampling of ozone. During the intervals between pulses, the ozone concentration will build up in the membrane layer. Once the potential pulse is applied, a certain amount of ozone will be consumed and the transient current, i, will be solely dependent on the permeability of ozone in the membrane layer. At a constant pluse frequency, a quasi-steady state is established for a given temperature and mixing conditions in the test solution.

EXPERIMENTAL

Electrode Design. The basic design features of the electrode systems used in this investigation are shown in Figure 1. The working electrode is a gold ring separated from the test solution by a gas permeable membrane. A thin film of electrolyte solution is held between the membrane and the electrode. A lens paper tissue is used to immobilize the electrolyte film. Vycor glass was used to isolate the reference and counter electrodes from the electrolyte layer. Two basic designs were used in this study. The two-electrode system (Figure 1a) was used for steady-state measurements. The three-electrode system (Figure 1c) was used for controlled potential pulse voltammetry, and for monitoring the ozone concentration under steady-state conditions during the pulse studies. The state-of-the-art on voltammetric electrode systems has been reviewed by Flato (*16*).

Apparatus. A Princeton Applied Research Model 174 Polarographic Analyzer was used for elerctrode polarization and current monitoring at steady-state conditions. A Transient Current Monitoring and Electrode Characterization System developed in combination with the Department of Electrical and Computer Engineering of The University of Michigan (*17*) was used for all pulsed potential experiments. For linear sweep voltammetry the initial potential was set at +1.2 V vs. Ag/AgCl. The potential was scanned in a cathodic direction at a sweep rate of 2 mV/s. Current was recorded on either a Houston Omnigraphic Model 2000 x-y plotter, a Hewlett-Packard Model 7100B strip chart recorder, or a Tektronix, Inc. Type 564 Storage Oscilloscope. Ozone was generated by either a Supelco, Inc. Type BC-10 or a P.C.I. Ozone Corp. Model C2P-6C ozonator using a dry oxygen feed and was introduced to the experimental solution through a coarse frit sparger. The exhaust gas was bubbled through two scrubbers filled with 20% KI.

The membranes used were homogeneous polymeric and microporous types. This included a 1-mil silicone rubber membrane Dimethylsilicone (General Electric Company), a 5-mil silicone rubber membrane Silastic sheet (Dow Corning Corporation), and a microporous polypropylene membrane Celgard 2400 (Celanese Plastic Company).

The flow system utilized for pulse studies is shown in Figure 2. It consisted of an ozonator, a contact chamber, an ozone monitoring cell, a peristaltic pump, and a jet nozzle for stirring the test solution. All components were connected together using $^5/_{16}$-in. Tygon tubing. A Manostat Varistaltic Pump, Advanced Model, was used to circulate the ozonated water back to the contact chamber (4-L Pyrex reaction flask with cover).

Measurement Procedures. Prior to its use, the perchloric acid supporting electrolyte was bubbled with ozone for 30 min and then purged with nitrogen for an additional 30 min. The lens

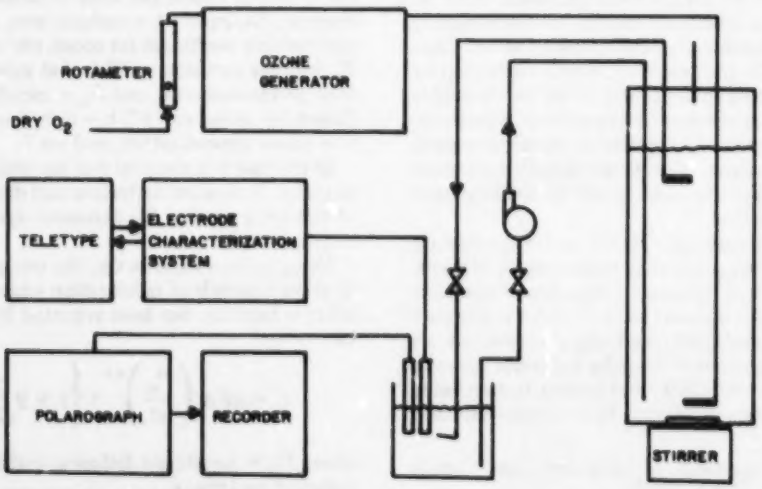

Figure 2. Experimental setup used for pulse studies

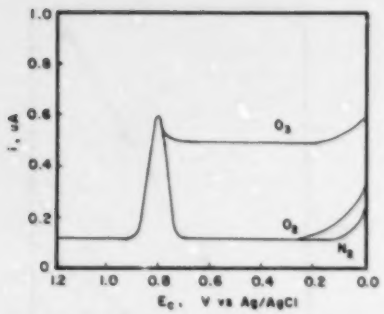

Figure 3. Linear voltage scan on a bare gold ring cathode in the presence and absence of oxygen and ozone in 0.1 m $HClO_4$

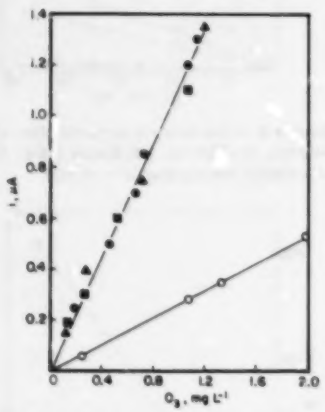

Figure 4. Calibration curves for voltammetric membrane ozone electrode using silicone rubber membranes: Independent runs during a 48-h period, (▲,■,●) 1-mil membrane; (○) 5-mil membrane

paper, used to immobilize the electrolyte layer was soaked in the same solution and treated in a similar manner.

Prior to the initial use of the electrode, it was necessary to precondition the electrode for 5 min at a constant potential of 600 mV vs. Ag/AgCl. This was required to reduce the surface oxide layers on the cathode. A constant stirring was maintained during both steady-state and pulse measurements. Between measurements and daily experiments the electrode was kept polarized and stored in distilled water.

In the pulse mode, the desired pulse train (duration and interval) was applied for a total of 50 pulses and the current sampled at the end of each pulse during the last 10 pulses. This allowed the measurement of the current at a point where the system has reached a quasi-steady state. All pulse-current values reported represent the average of 10 measurements. During the total span of the pulse study (24 h on a continuous basis) the ozone concentration was monitored at steady-state conditions using a second ozone electrode, previously calibrated. The test solution was also analyzed for ozone using a differential pulse polarographic (DPP) technique based on the reduction of phenylarsine oxide (PAO) (*18*) or an iodometric microtitration technique (*3*).

RESULTS AND DISCUSSION

Preliminary experiments were conducted by applying a linear voltage scan to the bare electrode in 0.1 M $HClO_4$. Typical results, shown in Figure 3, were obtained in the presence and absence of ozone. These findings are identical to those reported earlier by Johnson et al. (*6*). The reduction of ozone does not occur until a gold oxide layer has been reduced as shown by the current peak at 0.8 V in Figure 3. Accordingly, the applied potential for voltammetric measurement of ozone was chosen at +0.6 V vs. Ag/AgCl.

Steady-State Techniques. In search of a suitable membrane, materials used with oxygen electrodes, such as polyethylene, Teflon, and polypropylene, were found to have insufficient permeability to ozone. Dimethylsilicone rubber was investigated since it exhibits a much higher permeability to most gases (*19*). Results using 1-mil and 5-mil thick silicone membranes are shown in Figure 4. These data were accumulated over a 48-h time period and show the stability as well as the linearity of response. The electrode sensitivity, calculated by linear regression analysis, was 0.87 $\mu A\ mg^{-1}\ L$ and 0.27 $\mu A\ mg^{-1}\ L$ for 1-mil and 5-mil membranes, respectively.

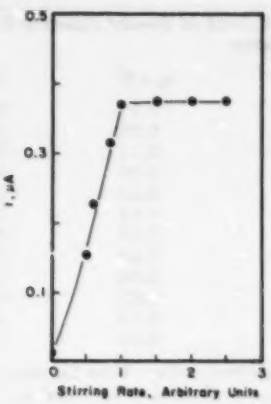

Figure 5. Dependence of steady-state response on the rate of solution stirring. Silicone rubber membrane; b = 5 mils

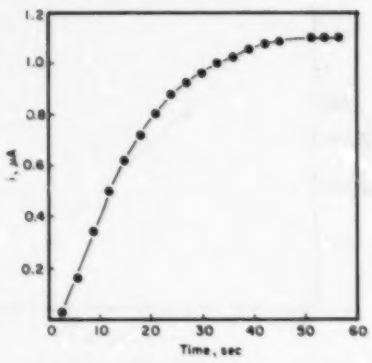

Figure 6. Attainment of steady response. Silicone rubber membrane; b = 5 mils

Generally, microporous membranes have much greater permeabilities than homogeneous membranes but suffer from the disadvantage that eventually they will exhibit slower rates of mass transport. If the membrane is sufficiently hydrophobic and the sample solution does not contain surface active materials, the membrane lifetime is somewhat longer. Results similar to Figure 4 taken over 48 h using a 1-mil hydrophobic microporous polypropylene membrane showed a sensitivity of 0.50 $\mu A\ mg^{-1}\ L$.

Effect of Stirring. The effect of stirring rate on the electrode sensitivity is shown in Figure 5. From an initial low current with no stirring, the response increased with increasing rate of stirring until a steady-state response was observed. This points out the need for adequate stirring to maintain the ozone concentration. A submersible stirrer will have to be used with the steady-state electrode for in situ monitoring.

Response Time. The experimental electrode response time was investigated with the 5-mil silicone rubber membrane. The electrode was polarized and the base-line current was recorded for distilled water; then the electrode was transferred to a solution containing ozone while stirred at a constant rate. Under these conditions the electrode showed 90% steady-state response in 33 s, as shown in Figure 6. These data are shown in Table I. The 90% response time for the 1-mil membrane

Table I. Attainment of Steady State for 5-mil Silicone Rubber Membrane

t, s	i_t, μA[a]	i_t/i_{ss}
9	0.17	0.31
12	0.25	0.46
15	0.31	0.56
18	0.36	0.66
21	0.40	0.73
24	0.44	0.80
27	0.46	0.84
30	0.48	0.87
33	0.50	0.91
36	0.51	0.93
45	0.54	0.98
∞	0.55	1.00

[a] b = 5-mil silicone rubber, Dow Corning Corp, "Silastic". $D_m = 1.6 \pm 0.1 \times 10^{-6}$ cm² s.

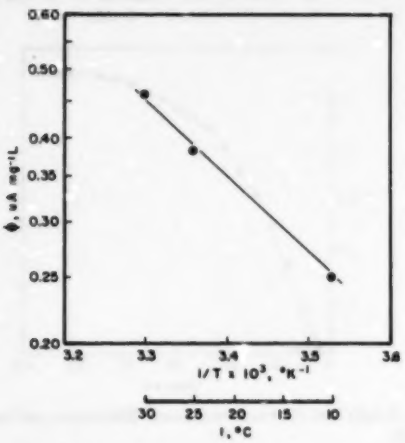

Figure 7. Effect of temperature on the steady-state voltammetric membrane ozone electrode sensitivity. Silicone rubber membrane; b = 5 mils

was 7.0 s as determined under identical experimental conditions as those used to obtain Figure 6.

Effect of Temperature. Since membrane electrodes with homogenous polymeric membranes generally exhibit large temperature coefficients, an investigation of temperature changes on the voltammetric membrane ozone electrode sensitivity was undertaken. The residual current was essentially constant over several orders of magnitude of temperature change, varying less than 30 nA. Increasing the temperature above 40 °C caused the anodic residual current to increase in an exponential manner.

Calibration curves for the electrode were obtained at three different temperatures using a 5-mil silicone rubber membrane and the sensitivities calculated by linear regression analysis. The sensitivity increased from 0.25 μA mg^{-1} L at 10 °C to 0.48 μA mg^{-1} L at 30 °C. A plot of the logarithm of the sensitivity at a given temperature vs. the reciprocal of that temperature (K) resulted in the expected linear relationship as shown in Figure 7, as reported earlier for membrane electrodes by Mancy et al. (*15*).

Pulse Techniques. Preliminary studies showed that the 1-mil membrane suffered degradation when continuously exposed to 0.2–0.6 mg L^{-1} of ozone for a period of 24 h. For this reason, the more resistant 5-mil membrane was selected for this section of the study.

Two different ranges of pulse durations were applied for each one of the five different pulse intervals considered. In the short range of pulse duration, 15–75 ms, a nonlinear response was observed in all cases. Similar results were observed for oxygen electrodes (*17*). The long range, 100–800 ms, consistently exhibited linear responses for pulse intervals above 1000–2000 ms as shown in Figure 8.

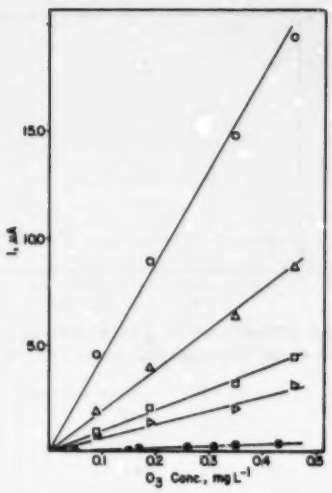

Figure 8. Influence of pulse duration on sensitivity: (○) 100 ms, (△) 200 ms, (□) 400 ms, (▷) 800 ms, (●) steady state. Pulse interval = 5.00 s. Silicone rubber membrane; b = 5 mils

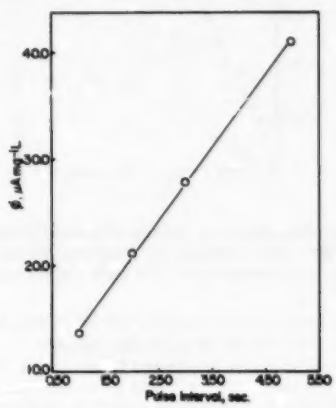

Figure 9. Sensitivity dependence on pulse interval. Pulse duration = 100 ms. Silicone rubber membrane; b = 5 mils

Table II. Effect of Pulse Duration on the Pulsed Voltammetric Membrane Ozone Electrode

pulse duration, ms[a]	φ, μA/mg O_3/L[b]
100	41.0
200	38.3
400	9.28
800	6.17
steady state	0.83

[a] Pulse interval was held constant at 5 s. [b] All currents were measured after quasi-steady state was obtained for duration interval selected.

The sensitivity observed for steady state operation was 0.83 μA mg L^{-1} and it increased with decreasing pulse duration as can be seen from Figure 8 and Table II. For a measuring mode of 100-ms pulse duration and 5-s pulse interval, a 49.5-fold increase in sensitivity, compared to the steady-state voltammetric membrane ozone electrode, was observed.

The effect of the pulse interval on the current is shown in Figure 9. Small pulse intervals obviously did not allow enough time for ozone replenishment to the membrane. The independence of sensitivity from pulse interval was not reached at any of the pulse intervals studied.

Table III. Comparison of Ozone Measurements with the Voltammetric Membrane Ozone Electrode and DPP of PAO

tap water[c]		river water[d]		secondary sewage effluent[e]	
$[O_3]^c$	$[O_3]^b$	$[O_3]^a$	$[O_3]^b$	$[O_3]^a$	$[O_3]^b$
0.37	0.32	0.29	0.47	0.11	0.20
0.67	0.74	0.32	0.32	0.25	0.39
1.03	0.15	0.49	0.73	0.33	0.43
1.26	1.65	0.55	0.99	0.35	0.65
		0.96	1.28	0.53	0.95
				0.76	1.05

[a] Concentration determined by DPP and PAO. [b] Concentration determined by electrode. [c] pH reduced to 6.5. [d] pH 8.5. [e] pH reduced to 7.3.

Applications. The application of the voltammetric membrane ozone electrode with a 5-mil silicone rubber membrane was investigated for the ozonation of tap water, river water, and secondary sewage effluent. All the samples were dechlorinated prior to ozonation and the ozone electrode was calibrated in distilled water using the DPP of PAO. Steady-state current was linear with concentration as determined by linear regression analysis of these data. The electrode was placed in ozonated solution and the current was recorded. A comparison of ozone measurement using the electrode and DPP of PAO is given in Table III.

In all cases the electrode measurements were greater than those determined by DPP of PAO for the same solution. This discrepancy is due to ozone decomposition during the time lag associated with sample fixing during the PAO procedure. Since electrode measurements are essentially instantaneous, they should represent the actual ozone concentration at any time. The discrepancy between the two methods was more pronounced in the sewage and river water than in the tap water. It was also necessary to lower the pH of the sewage and tap water, as noted in Table III, before residual ozone could be maintained and measured. This was necessary since ozone is highly unstable at high pH values (*20*).

Using an experimental arrangement similar to that of Figure 2, a microprocessor-controlled electrode characterization system was programmed to automatically regulate the rate of ozone production based on electrode measurements. The control of ozonation processes based on the in situ measurement of residual ozone is one of the most promising applications of the electrode system and is currently being developed by our laboratory.

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